# CEMENT AND LIME MANUFACTURE

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## Determination of Particle Size Distribution.

In the course of a paper on sedimentation methods for determining the size distribution of finely pulverised materials, Mr. H. E. Schweyer, of Columbia University, New York, describes a special pipette which requires only 15 minutes settling time plus the time required to recover the dried sample. One hydrometer may be used for as many analyses as can be performed expediently and all may be carried to completion, whereas a separate pipette is required for each analysis.

The weight distribution is determined by direct weighing of the residue from a pipetted sample. The diameter of the particles remaining in suspension is computed from the direct measurement of the height of fall. The apparatus used is the Andreasen pipette or the special pipette for rapid analysis illustrated in *Fig.* 1.

**Preparation of Sample.**—A sample containing a known dry weight sufficient to give a 1 or 2 per cent. suspension is used for materials of density equal to about 3 gr. per c.c. If the material is of higher density, a proportionately larger concentration should be used, but if it is of lower density a 2 per cent. suspension is sufficient to obtain precision in the low concentrations at small diameters.

A stock dispersing solution containing 10 gr. of sodium metasilicate (" Metso Granular ") per litre of distilled water should be made. Forty c.c. of this stock solution are added to the sample in a 600-c.c. beaker and allowed to stand a few minutes. The volume is then made up to about 500 c.c. with distilled water. The beaker and contents are then placed under the stirring apparatus (*Fig.* 2) and sufficient water added to cover the top of the stator. In this apparatus the propeller is encased in a perforated brass stator; this stator aids in producing shearing action and prevents any swirling motion which does not give good dispersion. The rotor should be close enough to the bottom of the beaker to prevent any dead spots, especially when using dense materials, and the level of the

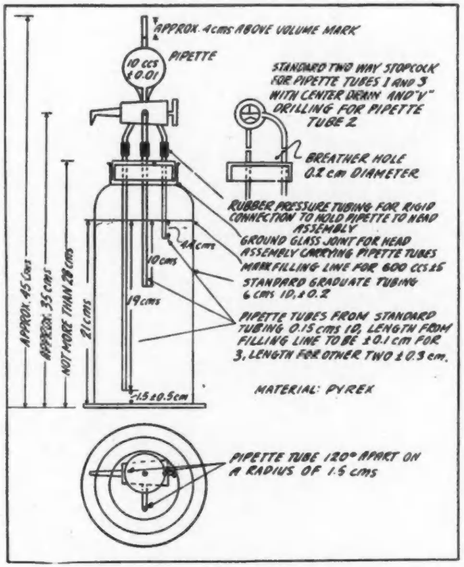


Fig. 1.—Pipette for Rapid Analysis.

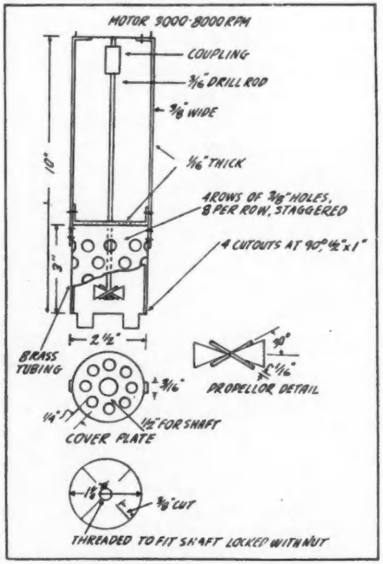


Fig. 2.—Stirring Apparatus for Coarser Particles.

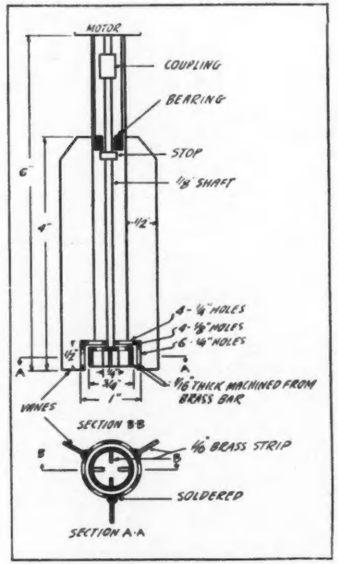


Fig. 3.—Stirring Apparatus for Very Fine Particles.

liquid should be above the rotor at a sufficient height to prevent the rotor from drawing air into the suspension. The time of dispersion should be 15 minutes and the suspension washed into the pipette cylinder. When the pipette head is inserted, the level of the suspension rises and accordingly distilled water is added to bring the level to a reference mark after the pipette head is inserted. This level (bottom of meniscus) becomes the starting level mark for every analysis and determines the starting volume of suspension for subsequent calculations. The pipette tubes should be empty and the stopcock closed when the pipette is inserted. All dimensions of the pipette necessary for computation should be obtained by calibration, and for best results the pipette and distilled water should be brought to the test temperature before starting.

**Test Procedure.**—Rubber tubing containing a glass tube of one bore for a mouth-piece is attached to the pipette and the apparatus assembled after dispersion. The level may be raised to the mark by adding water through the breather-hole. With the breather-hole closed by the finger the entire assembly is given an end-over-end motion. The exact time at which this motion is stopped is noted and the assembly placed in the constant-temperature bath and clamped to a ring-stand to prevent disturbance during the sampling manipulations. The constant temperature bath should be thermostatically controlled and of sufficient depth to surround the pipette body for 2 to 3 cm. above the starting-level mark.

At exact time intervals samples are withdrawn as follows. (The proper time intervals to get a representative distribution curve will depend upon the density and the size distribution.) Since it takes about 15 seconds to siphon the sample, the midpoint of this interval should be used for calculating particle size. A continuous suction should be applied (by mouth) and the pipette filled, after which the stopcock is closed and the fluid allowed to run immediately into a weighed crucible held under the drainage spout. Because of the construction of the stopcock, proper manipulation must be used to prevent runback. Pressure should be applied to blow out the sample at high velocity until the pipette is about half empty. At that time a slight suction should be applied to bubble air back through the drainage spout and the remaining sample, thereby washing the walls of the pipette ; pressure is again applied and the remaining part of the sample blown out. Care should be taken not to draw out more than the exact amount wanted and also that the stopcock is closed immediately after the sample reaches the mark on the pipette. Any pumping back and forth allows the coarse particles to settle out of the pipette. The drainage spout should be held against the side of the crucible to prevent splashing. After the pipette has been blown out, it should be allowed to drain for a few seconds and any further drainage blown into the crucible. The stop-cock is then opened and the suspension allowed to seek its own level in the pipette tube. No other washing is necessary as any error caused by adherence on the sides is well within the limit of experimental error for most materials.

For very fine materials the samples must be taken somewhat more slowly and carefully to prevent siphoning off of material below the pipette stem. The siphoning off of these particles has relatively little effect for coarse materials, but

for fine materials may give results showing more than 100 per cent. remaining in suspension.

The crucibles used for collecting the samples may be ordinary porcelain or Gooch crucibles with asbestos mats, and suction-filtering procedures may be used where there is present no material sufficiently fine to pass the mat. Fritted glass filters might also be used for this purpose. The crucibles may be dried in an oven at any convenient temperature up to 140 deg. C., which requires from one to two hours depending upon the procedure used. For very rapid results platinum Gooch crucibles may be employed, the asbestos mat being dried over a direct flame before and after sampling. This method, however, is not suitable for materials containing volatile constituents or materials subject to decomposition at high temperatures. The crucibles should be weighed to the nearest 0.1 milligramme.

Suggested sampling times for most materials and a 19-cm. to 20-cm. starting height are 1, 3, 8, 30, 120, 480 and 1,440 minutes. If the special pipette is used, the time for analysis is materially reduced since the same results can be obtained in four hours instead of 24. Sampling procedure for the special pipette is shown in *Table I*.

TABLE I.

| Sample No. | Tube No. | Time (minutes) | Diameter* (microns) |
|---|---|---|---|
| 1 | I | 1 | 53·00 |
| 2 | I | 3 | 30·00 |
| 3 | I | 7 | 20·00 |
| 4 | II | 15 | 10·00 |
| 5 | II | 45 | 5·00 |
| 6 | III | 60 | 2·50 |
| 7 | III | 240 | 1·25 |

* Actual diameter depends upon the particular liquid-solid system used. Refer to Equation (2).

## Calculations.

(a) Measurement of concentration of particles remaining in suspension.—In this method the computation of the percentage remaining in suspension ($G_e$) after a given time is obtained by the formula

$$G_e = \frac{100 V_c w}{V_p W} = Kw \quad \ldots \quad (1)$$

where $V_c$ is the volume of the suspension at the start in c.c.s, $w$ is the weight of dried material in grammes in a pipetted sample of $V_p$ cubic centimetres, and $W$ is the dry weight of the sample taken at the start in grammes. The constant $K$, for convenience in computing, may be made equal to 1,000 by varying the weight of the sample $W$, according to the calibrated volumes of the pipette and cylinder.

Calculation of size or particles remaining in suspension.—The size of particles remaining in suspension after time $T$ in minutes from the start of the test is given by the following form of Stokes' Law.

$$d = \sqrt{\frac{307 \times n \times h}{(D_s - D_1) \times T}} \text{ microns} \quad \ldots \quad (2)$$

where $d$= equivalent spherical diameter, $n$= viscosity (centipoises), $h$=height of fall (cm.), and $D_s$ and $D_1$ are densities of the solid and liquid respectively in grammes per c.c.

The value of $h$ for successive samples decreases, and in any given pipette is fixed by calibration. That is, any consecutively numbered sample starting from the first one withdrawn is always the same height for the same consecutive sample in any other determination. Values for the density and viscosity of the suspending fluid described to be used in equation (2) are given in *Table II*.

TABLE II.

| Temperature (deg. F.) | Density/4 ($D_1$) | Viscosity ($n$) |
|---|---|---|
| 67 | 0·9986 | 1·00 |
| 72 | 0·9980 | 0·95 |
| 77 | 0·9974 | 0·90 |
| 82 | 0·9967 | 0·85 |
| 86 | 0·9960 | 0·80 |

A plot of cumulative percentages undersize versus log diameter allows interpolation of the amount below any size. If combined sieve analysis is used with pipette analysis, the point of separation for the No. 325 sieve data may be assumed to be 53 microns. This is 1·2 times the sieve aperture, and the same relation may be employed for larger size sieves if desired.

## "The Concrete Year Book."

THE 1943 edition of "The Concrete Year Book" (edited by Oscar Faber, O.B.E., D.Sc., M.Inst.C.E., and H. L. Childe) is now ready (price 5*s.*; by post 5*s.* 8*d.*). The volume, which is now in its twentieth year, comprises 790 pages, and, as usual, includes a Handbook of information of everyday use to those engaged in concrete design and construction; a complete Directory of the concrete and allied trades and professions, and an extensive Catalogue illustrating and describing businesses, materials, and plant engaged in or used in the concrete and allied industries. The Handbook has been revised and brought up to date, and has new features, including new wartime uses of concrete and reinforcement tables. The Directory, revised up to December, 1942, gives temporary wartime addresses. Copies may be obtained from Concrete Publications, Ltd., 14, Dartmouth Street, Westminster, S.W.1.

# Properties of Lime for Industrial Purposes.

## The Rate of Settling.

SOME useful notes on the determination and measurement of the properties of lime for use in industrial processes are given by Mr. R. W. McAllister, who is in charge of research work for the National Lime Association of America. In the course of a paper on the work being undertaken, Mr. McAllister says:

A knowledge of the settling characteristics of a hydrate suspension is of great value in understanding the potential use of any lime or hydrate for a great number of commercial applications. This test, which is simple in operation, presents a general picture of the broad fields of use of any hydrate under consideration.

A 10-g. sample of hydrate is placed in a 100-c.c. graduated flask and wetted with water for 30 minutes. The hydrate is then thoroughly suspended in water at 25 deg. C. to a total volume of 100 c.c. and the settled volume recorded at intervals until no further settling takes place. In carrying out the test on quicklime, 7.5 g. are hydrated under predetermined conditions (boiling water is preferred) and, when the temperature has dropped to 25 deg. C., the suspension is made up to 100 c.c. with water at the same temperature. Under these conditions the settled volume of a soft-burned lime or hydrate after one hour will range between 50 and 80 c.c., while that of a hard-burned hydrate will be between 20 and 50 c.c. Similarly the final settled volume of a soft-burned hydrate will usually be about 30 to 40 c.c., while for a hard-burned product it will be 20 to 30 c.c.

The settled volume after one hour is of great value in determining the suitability of lime for uses such as causticising and leather treating, since in the former instance rapid settling is important, while in the latter slow settling is of equal importance. In fact, for the majority of industrial uses the rate at which the hydrate settles from water and the volume which the settled hydrate assumes are very important. The settling rate appears to be affected by the size, shape and state of aggregation of the hydrate particles. The settled volume appears to be correlated with average particle size, rate of reactivity, surface area and plasticity.

The settling rate and settled volume can be modified by many factors. In general, with high-calcium limes, it can be said that the harder it is burned the faster the resulting hydrate will settle. Likewise, the closer a certain temperature of hydration is maintained with the use of an excess of water (up to a certain point) during hydration, the slower the resulting hydrate will settle.

Certain chemicals added to hydrate markedly alter the resulting volume. This is shown by *Table I*.

Hydrates A and B have the same chemical analysis and were derived from the same high-calcium limestone. Their very divergent settling rates indicate the differences which may result from different methods of burning and hydration. Hydrate A observed microscopically is extremely porous, has irregular edges, and an average particle approximately 2 microns in diameter. Hydrate B, on

TABLE I.
EFFECT OF CHEMICALS ON SETTLING RATES OF HYDRATE

| | Settled Volume at Indicated Time | | | Final Time |
|---|---|---|---|---|
| | 30 min. | 1 hr. | 2 hrs. | |
| Hydrate A | 90 | 78 | 45 | 39 |
| Hydrate A + 1% Nopco 1111 | 67 | 57 | 55 | 54 |
| Hydrate A + 1% Sapamine KW | 62 | 44 | 35 | 27 |
| Hydrate B | 65 | 35 | 27 | 27 |
| Hydrate B + 5% Nopco 1111 | 42 | 42 | 41 | 41 |
| Hydrate B + 1% Sapamine KW | 31 | 22 | 22 | 22 |
| Hydrate A + 30 c.c. Tertiary buryl alcohol | 99 | 99 | 98 | 97 |
| Hydrate A + 2% Carbon dioxide | 95 | 95 | 95 | 95 |

the other hand, has smooth edges, less porosity, and an average particle diameter of 5 microns. Nopco 1111 is a so-called anionic wetting agent and consists of a mixture of 50 per cent. coconut oil in 50 per cent. sulphonated olive oil. Sapamine KW is a cationic wetting agent comprising diethyl amino ethyl stearyl amide acetate. Many other wetting agents markedly affect the settling rate and settled volume of hydrate. These two are given to illustrate the range of effect which may be obtained.

It is thought that the non-settling product obtained by the action of carbon dioxide on lime hydrate consists of a hydrous carbonate, since in appearance it is definitely gell-like and will keep the indicated settled volume for weeks. However, if the suspension is repeatedly shaken it will finally settle to a smaller volume such as 49 c.c. It should be noted, however, that not all hydrates will form this slow-settling material with carbon dioxide.

There are methods of altering the rate at which a specified hydrate settles from a water suspension. It is possible by air classification, or otherwise, to separate the smaller from the larger particles ; the separated products then will differ from the original hydrate and each other in settling characteristics. By mechanical disintegration a very pronounced effect upon both settling rate and settled volume can be obtained. The temperature of the water in which hydrate is suspended also has a significant effect upon the settling characteristics.

### Settling Characteristics of Dolomitic Hydrates.

Conditions during the burning and hydration of high-calcium lime which will produce a fast or slow settling hydrate cannot be employed to yield a dolomitic hydrate with like characteristics. Furthermore, dolomitic limes appear to vary greatly in their settling characteristics when burned and hydrated under identical conditions. Thus some dolomitic limes burned at increasing temperatures become progressively faster settling and show lower settled volumes, as do the high calcium limes. Others, however, reverse this trend and yield the slowest settling and largest putty-volume hydrates when burned at 2,500 deg. F. for long periods. It thus appears that the optimum conditions to produce a certain type of hydrate

must be determined for each lime. The only conclusion which has been tentatively drawn is that when the $SiO_2 + R_2O_3$ content of the dolomitic stone is low the conditions effective with high calcium limes appear to apply. When the $SiO_2 + R_2O_3$ content is high, the higher temperature of burning gives slower settling and longer-settled-volume hydrates.

### Surface Area.

The surface area of a hydrate is important for applications such as in water-treating, bleach manufacture, soda-lime, etc. It is an even better index of reactivity than particle size, since it takes into consideration both shape and porosity and is not influenced by the state of aggregation. After exploring several methods which might be suitable for application with hydrate, the nitrogen absorption method was selected as appearing most satisfactory. This method depends upon the fact that under suitable conditions nitrogen will form a mono-molecular layer on the surface of finely divided materials. The amount of nitrogen forming such a layer can then be measured. Since it is known that each cubic centimetre of nitrogen will cover a surface of 43,800 sq. cm., the surface area can be determined. A soft-burned commercial high-calcium lime hydrate by this method of testing showed a surface area of 43,500 sq. cm. per gramme (21,200 sq. ft. per pound). When this hydrate was subjected to dry mechanical disintegration so that the average diameter of the particle was reduced by approximately one-half, the surface area, instead of being at least twice as great, increased only from 43,500 to 46,000 sq. cm. per gramme. Microscopic examination of the hydrate before and after disintegration has helped to explain this apparent discrepancy since little change in actual size of crystals occurs, but instead crystal clusters or aggregates are broken down into smaller groupings. Thus little actual surface area increase would be expected.

Surface area measurements using liquid nitrogen carried out on completely hydrated dolomitic hydrate gave a value of 115,000 sq. cm. per gramme. Thus this product has over 2½ times as great a surface area as even a soft-burned high-calcium hydrate. This difference in surface area may serve to explain the difference in plasticity which commonly exists between these two types of hydrate.

Microscopic examination of dolomitic hydrates shows an undetermined amount of particles considerably below 1 micron in diameter, which presumably are magnesium hydrate. It is possible that such small particles serve to lubricate the larger particles and thus impart the elusive characteristic of plasticity.

Since surface area measurements show the amount of surface exposed to any liquid-reacting surface, and therefore the value of hydrate for any rapid-reaction use, a knowledge of the effect of burning and hydration conditions upon surface area of the resulting hydrate would appear to be worth investigation.

### Abrasiveness.

The abrasive quality of lime or hydrate is very important in some uses. Thus in oil treating, where lime is passed as a suspension through pipes and valves, the cost of valve and pipe replacement is important. In agricultural sprays con-

taining lime hydrate differences in the abrasiveness of hydrates is very important. In wire drawing the abrasiveness of hydrate affects the life of the die as well as the tendency of the wire to break. A lime or hydrate of low abrasive quality is essential in causticising when the sludge is to be used for paper coating if excessive wear to the paper rolls is to be avoided.

In an effort to find a unit of measurement which would permit comparison of the abrasiveness of hydrates a machine is used which has an electric motor-driven rotating steel plate upon which a thick layer of paraffin is placed. The lime hydrate is made into a slurry with ethylene glycol and poured upon the rotating paraffin surface. A weighed silver block held in a fixed arm is then arranged to cause the silver to rest on the paraffin surface lubricated by the hydrate slurry. An adjustable weight on the arm can be moved to increase or decrease the amount of pressure. The machine is provided with a counter and is usually run for 2,000 to 5,000 revolutions of the disc. The resulting loss in weight of the silver block is used for comparing abrasiveness. At the completion of a test the hydrate slurry is wiped off and the paraffin surface scraped with a knife to present a fresh surface for the next test. In view of the wide variation in abrasiveness between various commercial products, this factor should be given more consideration by both makers and users of hydrate.

Whereas the silica content of a product has frequently been considered an indication of abrasiveness, this is not justified. Thus, silica present as $SiO_2$ is extremely abrasive, whereas that present as clay (aluminium silicate) is much less abrasive. Either form of silica may contribute abrasiveness to lime when temperatures high enough to permit fusion occur during burning. With certain stones it is possible to produce a non-abrasive hydrate by soft burning the stone and separating the silica after or during hydration. Such non-abrasive hydrate can be shown to contain a significant amount of residual silica, doubtless as clay.

Another specification sometimes employed to indicate relative abrasiveness, which does not appear justified, is the sieve-size specification. Commercial hydrates from some rotary kilns show 10 to 15 per cent. retained on a 300-mesh screen have lower abrasion numbers than others having less than 2 per cent. Examination of the residues has shown that rotary kiln hydrates frequently become balled or compacted together and such balls are retained on fine-mesh screens. Such balled particles may be and frequently are non-abrasive, being entirely unlike the sandy material which may be screened from other hydrates.

### Hydrate Adhesion.

For certain lime hydrate applications the adhesion or bonding of the hydrate to a metallic surface is important. Thus, in wire drawing a satisfactory hydrate must adhere to a wire surface to assist in lubricating the die as the wire passes through. Some hydrates exhibit little adhesion and readily flake off, which renders them unsatisfactory for this application. In an effort to establish methods to show the comparative suitability of hydrates for this application the angle of inclination was employed at which a steel ball rider will slide down an inclined steel plate. Three $\frac{3}{8}$-in. balls are clamped in a frame which is placed on a steel

plate and the angle of the plate altered until the rider just slides. The steel plate is then dipped into a 5 per cent. suspension of hydrate, placed in an oven at 110 deg. C. to dry, and the angle of slip again determined on the dry hydrate-coated plate. By this means it is possible to show the relative adhesiveness of various hydrates to steel surfaces. After each test the hydrate is thoroughly removed from the steel surface. The steel balls are rotated in the frame after each test to present a fresh surface to the plate. If the practice in a wire-drawing plant is to use a " sull " or slight rusting of the wire surface prior to the lime dip, the steel plate can be similarly treated. Using a rider of 110 grammes total weight, the inclination, using a polished steel plate, was 1⅞ inch per foot before the application of hydrate to the metal surface. With the more satisfactory wire drawing hydrates, the inclination was 4½ to 5½ in. per foot when a 5 per cent. suspension of hydrate was employed.

## Microscopic Examination of Hydrate.

Both soft-burned and hard-burned high-calcium hydrates have been examined under the ordinary microscope as well as under the electron microscope. Just what constitutes a typical particle of either hydrate is somewhat difficult to state with certainty. It is believed, however, that in soft-burned hydrate the particles are characterised by very irregular edges which cause the product to pack readily into aggregates. Very little evidence was found of crystalline structure in the particles, or, if crystalline structure exists, the particles are so small as to show no sharp edges under the magnification (8,500 diameters) employed. The particles of such hydrate normally have an aggregate size ranging between 0·5 and 5 microns, usually of fairly uniform cross-sectional area. Hard-burned hydrate, on the other hand, appears to consist of particles or aggregates of larger average diameter. The edges usually are sharper and there is evidence of less porosity. In some instances there is evidence of plate-like crystals.

When dry hydrate passes through a hopper or lime-feeding device the flow characteristics of the material may change very markedly. Thus, a free-flowing product may suddenly start to ball and cause trouble by arching in the chute. In a study of factors which might be responsible for this behaviour it was noticed that certain hydrates when shaken in a dry container develop a very pronounced electrostatic charge. The charge on some occasions is evident for a distance of 4 ins. from the hydrate container. Hydrates from the same source do not always exhibit this property.

It has not yet been possible to determine the factors responsible for this characteristic.

# Lime in the Paper Industry.

## PROPERTIES REQUIRED FOR MANUFACTURE OF CHEMICAL WOOD PULP.

IN a recent number of *Pit and Quarry*, Mr. A. M. Cadigan, a technical director of the St. Regis Paper Company, discusses the quality of lime suitable for the production of chemical wood pulp made by the sulphite, soda, and sulphate (Kraft) processes. The author points out that lime is used not always because it is the most desirable chemical but often because it is the most economical. When it is considered that 56 lb. of lime compare with 80 lb. of caustic soda and 106 lb. of soda ash in neutralising value, and that the cost per ton of the chemicals is about $12, $40, and $20 respectively, the economy is very evident. The characteristic that makes lime not always the most desirable chemical is generally the limited solubility of many of its compounds, while, on the other hand, advantage is taken of that characteristic in many stages of processing.

The quality of lime suitable for all purposes in the production of chemical wood pulp could be rather generally covered by one set of specifications, with one exception, namely, the dolomitic lime used in the milk-of-lime process of making "sulphite acid." It might be stated further that the limestone suitable for use in the sulphite acid tower system should be of such quality as to produce the specified lime without presenting any great operating difficulties.

These specifications are (in percentages) in general: Available lime (CaO), (minimum), 92·5; acid insoluble matter (maximum), 1 (preferably not over 0·8); mixed oxide ($Fe_2O_3+Al_2O_3$) (maximum), 0·8; magnesium oxide (MgO) (maximum), 2; ignition loss (maximum), 1; manganese compounds (maximum), trace. The tolerance of manganese compounds depends to some extent on the purpose for which the pulp is used. In "dissolving pulps," including pulps used in the textile industry, the presence of manganese salts is very undesirable. Manganese salts also act, perhaps catalytically, to decompose bleach liquor (calcium hypochlorite).

The lime should be light grey to white in colour, contain no char or other extraneous matter, and be free from an amount of dust that would cause discomfort to the workmen.

The specification for slaking rate requires that 200 gr. of the lime, as received, added to 300 millilitres of distilled water at 20 deg. C. (contained in an insulated cup) shall slake at such a rate that a temperature of 99 deg. C. will be reached in not over 80 seconds.

The settling characteristics are specified as follows. A suspension of a carefully slaked sample of the lime, as received, at a concentration of 30 to 32 gr. CaO per litre, added to a 250-millilitre graduated cylinder at a temperature of 37 deg. C. and thoroughly mixed shall settle to not over 40 per cent. of the initial height of the sludge after one hour of settling time; the final sludge (settling overnight) to be not over 20 per cent. of the initial height of the sludge. If the lime is to be used for bleach-liquor making, this settling test can be made much

more significant by carefully slaking a definite weight of lime, diluting to a concentration of 30 to 32 gr. of CaO per litre (as determined by titration), adjusting the temperature to, say, 27 deg. C., then chlorinating to a concentration of about 30 gr. per litre of available chlorine. Mix and transfer a portion to a 250-millilitre graduated cylinder, and determine the settling rate and the volume of sludge. Also, note the nature of the sludge, whether granular, colloidal, etc. Decant the supernatant liquor and test for free lime and available chlorine content. By testing this liquor at intervals of 24, 48 and 72 hours for available chlorine the stability of the liquor is determined as well as, indirectly, the presence or absence of appreciable amounts of harmful contaminants. In the chlorination of many limes a curdy precipitate that is more or less colloidal in character and slow settling is formed ; this is an undesirable characteristic and is made evident by this chlorination test. Such a test, modified to duplicate actual mill conditions, can serve almost as an " acceptance or rejection " test without further investigation.

The " available-lime " (CaO) content, since it is a measure of the lime available for reaction in such processes as causticization, etc., is of much greater significance than is the determination of the total calcium. It is conveniently determined by means of the " sucrose " method : Weigh out 1 gr. of a representative sample ground to pass a 100-mesh screen and add to a little water in a 300-millilitre Erlenmeyer flask. Boil for a few minutes until thoroughly disintegrated. Cool and add about 200 millilitres of water and 40 gr. of granulated sugar. Stopper the flask and mix the contents thoroughly by shaking every 15 minutes or oftener for a period of two hours. Filter by suction on a Buchner funnel and wash the residue three times with 10-per cent. sugar solution. Titrate the filtrate with 0·5 NHCl and phenolphthalein. Calculate the titration to CaO and report as " available lime." 1 millilitre 0·5 NHCl = 0·01402 gr. CaO.

The general stages common to all the processes of pulp manufacture are (1) Preparation of the wood ; (2) digestion (or cooking) of the chips ; (3) washing of the pulp ; (4) refining of the pulp ; (5) preparation of the pulp for marketing. In plants that bleach the pulp this stage takes place after the refining.

The wood is reduced to chips that are subsequently classified to proper length (usually about ¾in.). The chips are then digested, or " cooked," in digesters with different solutions that exert a solvent action on the lignin and other intercellular or cementing substances of the wood, bringing them into solution and liberating the cellulose fibres in a more or less pure form. These cellulose fibres constitute the " pulp." The contents of the digester are then blown into a tank, and various methods are used for removing the liquor as completely as possible from the pulp. The pulp, carried in a large volume of water, is now subjected to screening operations, and in the final stage in the manufacture of unbleached pulp the water is removed, the fibres are formed into a sheet and either sent through a wet press and sold as wet laps or put through a drying machine, cut into sheets, and sold in bales.

## The Sulphite Process.

In this process the chips are cooked in a solution of calcium bisulphite plus free sulphurous acid, called " sulphite acid." The two most popular methods of pre-

paring this " acid " are the " milk-of-lime " system and the " limestone-tower " system.

In the milk-of-lime system a burned lime containing a high percentage of magnesia (at least 40 per cent.) is slaked and diluted with sufficient water to produce a milk-of-lime having a strength of between 1 and 2 deg. Baumé. In the most commonly used system this milk-of-lime is pumped into the top compartment of a four-compartment tower, overflowing from this compartment into the next lower compartment, and so on down to the bottom of the tower. The bottoms of the different compartments consist of perforated copper plates, the perforations being rather small in order to ensure small gas bubbles and a consequently greater surface of contact. Cooled sulphur-dioxide ($SO_2$) gas is drawn through the milk-of-lime under vacuum or forced through under pressure, the gas passing through the small perforations up through the milk-of-lime. The resulting solution contains a predetermined amount of calcium-magnesium bisulphite (called combined $SO_2$) plus free sulphurous acid (called free $SO_2$). The reaction is :

$$Ca(OH)_2 + SO_2 = CaSO_3 + H_2O$$
$$Mg(OH)_2 + SO_2 = MgSO_3 + H_2O$$

On the further addition of $SO_2$,

$$CaSO_3 + H_2O + SO_2 = Ca(HSO_3)_2$$
$$MgSO_3 + H_2O + SO_2 = Mg(HSO_3)_2$$

Upon first adding the $SO_2$ the monosulphites of the bases are formed ; the calcium monosulphite, being insoluble, precipitates ; the magnesium salt is soluble. On further addition of $SO_2$ the bisulphites of the two bases are formed, both being soluble.

One of the reasons for the high magnesia content of the lime for use in this system is that the magnesium monosulphite and the magnesium sulphate (some of which is always formed during the process) are much more soluble than the corresponding calcium salts, and hence have less tendency to settle out and clog the perforations in the plates and form deposits in the pipe lines in case of low $SO_2$ content or other inefficiencies in the gas-producing operations. Another reason for the high magnesia content is that it is generally believed that the pulp produced by a high-magnesium-base acid is a softer, more flexible fibred pulp than that produced by a straight calcium-base acid. The reason an all-magnesium-base acid is not generally used is a matter of economy.

The specifications for lime for this purpose are as previously outlined for lime in general, with the exceptions that a high magnesia content is desirable and the rapid settling characteristics are not so vital.

Probably the most popular and most widely used method of preparing the " sulphite acid " is the " limestone-tower " system. In its most common form two concrete towers (sometimes three or four towers are used to obtain greater flexibility) are filled with limestone loosely piled on grates. Water is sprayed into the top of one tower and flows down over the rock to the bottom, whence it is pumped to the top of the second tower to flow down over the rock in that tower. Cooled

sulphur-dioxide ($SO_2$) gas is blown into the bottom of the second tower and, flowing counter-current to the water, is dissolved in the water, forming sulphurous acid which reacts with the limestone forming calcium bisulphite according to the reaction

$$CaCO_3+2SO_2+H_2O=Ca(HSO_3)_2+CO_2$$

The gas unabsorbed in its passage through the first tower is conducted to the base of the second tower and in its passage upward the absorption is completed. By means of gas seals and valves the operation of the towers can be reversed, in which case the weak-acid tower becomes the strong-acid tower, and vice versa. Because of the good absorption of the gas in the strong-acid tower, the gas entering the second tower is so weak that this tower can be charged with limestone during operation.

The limestone used in the towers should be a high-calcium rock with a low content of magnesium, although a rock containing not over 8 to 10 per cent. magnesium carbonate will work without any difficulty. Magnesium carbonate is less soluble in the acid than calcium carbonate, and while the latter is dissolved the magnesium carbonate remains in suspension for some time before it dissolves, in some cases forming a sludge on the stone and slowing up the reaction, thereby reducing the capacity of the towers. This sludge also tends to plug the grates, thus requiring frequent washing out.

As mentioned before, a limestone that would work most satisfactorily in the towers is one that would produce the lime specified in the original outline in this paper without presenting any great operating difficulties. The stone should be in blocks of such size as to be handled conveniently by one man and free of small pieces—3 in. and less—as these tend to plug the towers. To determine the suitability of stone for use in the towers the following practical test is of greater significance than a chemical analysis. Treat 25 gr. of small lumps representative of the limestone with 25 millilitres of 20-per cent. hydrochloric acid (HCl) at a definite temperature (20 to 25 deg. C.) in a beaker. Note the time of reaction, the nature (granular, colloidal, etc.) and colour of the insoluble matter and the rate at which it settles, and the colour and clarity of the supernatant liquor. Such a test has been found convenient where a survey is being made of different seams in the same quarry, or of limestone in different quarries.

It is important that the insoluble matter of a limestone used in pulp making be light in colour and rapid-settling.

The density of the stone used in the towers is also an item of interest, especially in mills that do not have refrigeration to maintain constant water temperature throughout the year. In summer, when the temperature of the water increases, a denser stone should be used than in the winter, in order to control the amount of "combined $SO_2$" (calcium bisulphite) in the acid. In many plants a fairly dense rock is used all the year round, steam being used to raise the temperature of the water during the winter. In sulphite mills making unbleached pulp, lime or limestone are used only in the acid-making stage.

## The Soda and Sulphate (Kraft) Processes.

These processes can be considered together since the lime serves the same relative purpose in both, namely, the causticizing of the " green liquor." In the soda process the solution (liquor) used for cooking the chips is a strong solution of the caustic soda, while that used in the sulphate process is a solution of caustic soda and sodium sulphide.

In both processes, after the cooking operation, the resulting strong " black liquor " is removed as completely as possible from the pulp, concentrated in evaporators and finally burned in furnaces of different types, the fused soda salts being caught and dissolved in a weak wash solution. This solution constitutes the " green liquor " and contains a high content of sodium carbonate. In order to make this solution suitable for cooking, it is necessary to convert the sodium carbonate to sodium hydroxide (caustic soda). This is accomplished by causticizing with lime according to the reaction

$$\underset{\substack{\text{sodium}\\\text{carbonate}}}{Na_2CO_3} + \underset{\substack{\text{calcium}\\\text{hydroxide}}}{Ca(OH)_2} = \underset{\substack{\text{sodium}\\\text{hydroxide}}}{2\,NaOH} + \underset{\substack{\text{calcium}\\\text{carbonate}}}{CaCO_3}$$

The calcium carbonate, being insoluble, is precipitated, and is removed from the liquor in most plants by settling, the supernatant liquor being drawn off to white-liquor storage tanks. It is important that the lime used in this operation be of such a nature that, in slaking, in order to present maximum surface, it breaks down into small particles, which, on reacting to form the calcium carbonate, coalesce to form large heavy particles that make for rapid settling to a sludge of the least volume, thereby ensuring the maximum yield of completely clarified white liquor. The presence of suspended calcium carbonate in the white liquor can cause irregularities in the cooking operation with consequent production of pulp of inferior quality in addition to the depositing of scale in pipelines and other equipment.

A lime such as that described in the original specifications has proved very satisfactory in the causticizing operation. However, in addition to the use of the right lime, it is also essential that certain conditions of manipulation and temperature be maintained constant and uniform in the operation if satisfactory results are to be obtained.

In most plants the calcium-carbonate mud is thoroughly mixed with a large volume of water and allowed to settle for the second time. The clear liquor resulting from this operation constitutes the weak wash used to dissolve the fused soda salts. In some plants the mud, somewhat diluted with water, is sprayed with water to remove as much soda salts as possible and then conveyed by screw-conveyors at a total-solids content of 50 to 55 per cent. to rotary lime kilns for the recovery of the lime. It has been indicated from experiments that by the recycling of lime through the causticizing-reburning-causticizing cycle and reburning at various temperatures, the recovered lime could causticize as well, producing a faster settling sludge than the corresponding new lime.

In addition to the regular tests mentioned previously, lime used for causticizing is often tested for " causticizing value." Such a test consists in taking a weighed amount of lime and boiling it for a given time in a solution of soda ash (sodium carbonate) of known concentration, containing more soda ash than can be causticized by the lime. The lime is allowed to settle and the clear liquor is tested for sodium hydroxide and sodium carbonate. From these data is calculated the amount of lime required to causticize a given weight of soda ash, this figure constituting the " causticizing value " of the lime. However, since the degree of reaction is dependent on the concentration of the soda-ash solution, many mills omit this test, considering the determination of available lime as being much more universally significant.

## Bleaching.

Soda and sulphite pulps can be bleached white by the use of calcium hypochlorite alone, but in order to bleach sulphate pulp to such a high white it is necessary to introduce one or two stages of chlorination into the bleaching process. By chlorination is meant the addition of chlorine gas directly into the pulp suspension. The residual acid remaining after the chlorination is usually neutralised with lime, although caustic soda is used to a limited extent. The common procedure is to make the bleach liquor as needed in the plant by adding chlorine gas to milk-of-lime. The general practice is to slake the lime and dilute to the required concentration ; then, keeping the milk-of-lime well agitated, chlorine gas is slowly added until the desired " available-chlorine " content is obtained. Care should be taken that the final temperature of chlorination does not exceed 37 deg. C., as beyond this temperature decomposition of the bleach liquor is apt to occur. The formation of bleach liquor takes place according to the reaction

$$2\ Ca(OH)_2 + 2\ Cl_2 = Ca(OCl)_2 + CaCl_2 + 2\ H_2O$$

Calcium hypochlorite ($Ca(OCl)_2$) is the active ingredient of the liquor. After chlorination the sludge is allowed to settle and the clear liquor (bleach liquor) decanted to storage.

The quality of the lime used for bleach-liquor making should be such as to meet the specifications previously outlined. Hydrated lime may be used, but usually under conditions where it is necessary to carry lime in storage to meet an emergency, or where bleach liquor is used only in limited quantities.